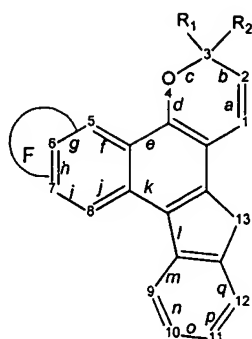


What is claimed is:

1. A photochromic naphthopyran having a central nucleus of the formula:

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wherein F is a 5-member, 6-member, or 7-member heterocyclic ring group having only one heteroatom, the heteroatom selected from the group consisting of oxygen, sulfur, and nitrogen, the 2,3 or 3,2 positions of the heterocyclic ring fused to the *g*, *h*, or *i* side;

R_1 and R_2 are the atoms or groups providing photochromic properties to the naphthopyran.

2. The photochromic naphthopyran of claim 1 wherein R_1 and R_2 are selected from the group consisting of aliphatic groups, aromatic groups, and heterocyclic groups.
3. The photochromic naphthopyran of claim 1 wherein R_1 and R_2 are selected from the group consisting of alkyl groups, aromatic groups, and heterocyclic groups.
4. The photochromic naphthopyran of claim 1 wherein R_1 and R_2 are selected from alkyl groups, phenyl groups, and naphthyl groups.
5. The photochromic naphthopyran of claim 1 wherein F comprises a dihydrofuran group.

6. The photochromic naphthopyran of claim 2 wherein F comprises a dihydrofuran group.

7. The photochromic naphthopyran of claim 3 wherein F comprises a dihydrofuran group.

8. The photochromic naphthopyran of claim 4 wherein F comprises a dihydrofuran group.

9. The photochromic naphthopyran of claim 1 wherein the 13-position has substituents R₃ and R₄, wherein R₃ and R₄ individually represent

a hydrogen atom,

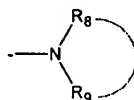
a hydroxy group,

a halogen atom,

a linear, branched, or cyclic C1-C6 alkyl, alkenyl, or alkynyl group,

a linear, branched, or cyclic C1-C6 alkoxy or alkenoxy group,

an amino group:



in which R₈ and R₉, which are the same or different, independently representing a hydrogen, a linear, branched, or cyclic alkyl group comprising 1 to 6 carbon atoms, an aryl or heteroaryl group, or representing (together with the nitrogen atom to which they are bound) a 5- to 7-membered ring which can comprise at least one other heteroatom selected from oxygen, sulfur and nitrogen, said nitrogen being optionally substituted with an R₁₀ group, which is a linear or branched alkyl group comprising 1 to 6 carbon atoms, a phenyl, a benzyl, or a naphthyl, an aryl or heteroaryl group selected from the group consisting of phenyl, naphthyl, phenanthryl, pyrenyl, quinolyl, isoquinolyl, benzofuranyl,

thienyl, benzothienyl, dibenzofuranyl, dibenzothienyl, carbazolyl,
indolyl,

a mono-substituted phenyl having a substituent at the para position that is
a linking group, $-(CH_2)_t-$ or $-O-(CH_2)_t-$, wherein t is the integer 1,
2, 3, 4, 5 or 6, connected to an aryl group, which is a member of another
photochromic naphthopyran,

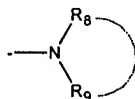
an aralkyl or heteroaralkyl group, the alkyl part of which is linear or
branched, comprising 1 to 4 carbon atoms,

a $-C(O)R_{11}$, $-OC(O)R_{11}$, or $COOR_{11}$ group, wherein R_{11} is hydrogen,
hydroxy, linear or branched C1-C6 alkyl, linear or branched C1-C6
alkoxy, phenyl, mono-substituted phenyl, naphthyl, mono-substituted
naphthyl, amino, mono(C1-C6) alkylamino or di(C1-C6)alkylamino,
e.g., N,N-dimethyl amino, N-methyl-N-propyl amino, morpholino,
piperidino or pyrrolidyl, said amino substituents being selected from the
group consisting of C1-C6 alkyl, phenyl, benzyl and naphthyl, and said
benzyl and phenyl substituents being C1-C6 alkyl or C1-C6 alkoxy,

a group $-OR_{12}$, wherein R_{12} is a C1-C6 acyl, an aralkyl or heteroaralkyl
group with a C1-C3 alkyl portion, a (C3-C7)cycloalkyl group, a (C2-
C4)alkyl group, or R_{12} is the group, $-CH(R_{13})R_{14}$, wherein R_{13} is
hydrogen or C1-C3 alkyl and R_{14} is $-CN$, $-CF_3$, or $-COOR_{15}$, wherein
 R_{15} is hydrogen or linear, branched, or cyclic alkyl, aralkyl or
heteroaralkyl,

a group $-CH(R_{16})_2$ wherein R_{16} is $-CN$ or $-COOR_{15}$,

a group $-CH(R_{15})R_{17}$, wherein R_{17} is $-COOR_{11}$, $-C(O)R_{18}$ or $-CH_2OR_{19}$,
wherein R_{18} is hydrogen, linear, branched, or cyclo-alkyl, aryl groups,
amino group of formula



R_{19} is hydrogen, $-C(O)R_{11}$, alkyl, alkoxyalkyl, phenylalkyl, mono-
alkoxy substituted phenyl-alkyl, or aryl groups,

a polyether, polyamide, polycarbonate, polycarbamate, polyurea, polyester residue, or a group ended by a polymerizable residue;

or R_3 and R_4 may together form a 3- to 7-member spiro-cyclic ring which can comprise at least one heteroatom selected from oxygen, sulfur, and nitrogen.

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10. The photochromic naphthopyran of claim 9 wherein,

(a) in the 5- and/or 8-position, a group R_6 is present wherein R_6 represents

a hydrogen,

a halogen, and notably fluorine, chlorine or bromine,

a linear or branched alkyl group which comprises 1 to 12 carbon atoms (advantageously 1 to 6 carbon atoms),

a cycloalkyl group comprising 3 to 12 carbon atoms,

a linear or branched alkoxy group comprising 1 to 12 carbon atoms (most advantageously 1 to 6 carbon atoms),

a haloalkyl, halocycloalkyl, or haloalkoxy group corresponding to the alkyl, cycloalkyl, alkoxy groups above respectively, which are substituted with at least one halogen atom, notably selected from fluorine, chlorine and bromine,

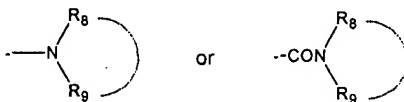
a linear or branched alkenyl or alkynyl group comprising 1-12 carbon atoms, preferably a vinyl or allyl group,

a linear or branched alkenoxy or alkynoxy group comprising 1-12 carbon atoms, preferably an allyloxy group,

an aryl or heteroaryl group having the same definition as that given above for aryl or heteroaryl groups within the definitions of R_3 , R_4 ,

an aralkyl or heteroaralkyl group, the alkyl group, which is linear or branched, comprising 1 to 4 carbon atoms, and the aryl and heteroaryl groups having the same definitions as those given above for R_3 , R_4 ,

an amine or amide group: $--NH_2$, $--NHR_8$, $--CONH_2$, $--CONHR_8$,



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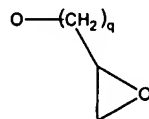
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R_8 , and R_9 having their respective definitions given for the amine substituents of the values R_3 , R_4 ,

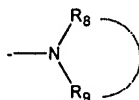
a $-C(R_{15})_2R_{11}$, $-OCOR_{15}$, or $-COOR_{15}$ group, wherein R_{11} and R_{15} are defined supra in R_3 and R_4 , a methacryloyl group or an acryloyl group, an epoxy group having the formula,



in which $q = 1, 2$ or 3 ,

a polyether, polyamide, polycarbonate, polycarbamate, polyurea or polyester residue, or a group with polymerizable residue,

- (b) in the 9-, 10-, 11-, and 12-positions there are at most 4 R_5 groups, each being the same as R_6 , defined hereinbefore; or
- (c) two adjacent R_5 together form a 5- to 7-member aromatic or non-aromatic ring which can comprise at least one heteroatom selected from oxygen, sulfur, and nitrogen, and/or at least one substituent selected from the group consisting of a C1 to C6 alkyl group which is linear, branched, or cyclic, a C1 to C6 alkoxy group which is linear or branched, and an amine group of formula $-NH_2$, NHR_8 , or

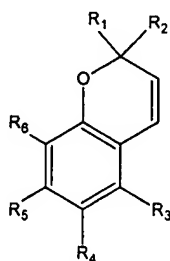


as defined in R_3 and R_4 for amine groups, said aromatic or non-aromatic ring can be optionally annelated with a benzene group.

11. The photochromic naphthopyran of claim 10 wherein R_1 and/or R_2 represent a para-substituted phenyl group, said substituents on the para-substituted phenyl group selected from hydrogen, alkyl, alkoxy, dialkylamino, diarylamino, or R_1 and R_2 together form an adamantyl group or norbornyl group or anthracenylidene group;

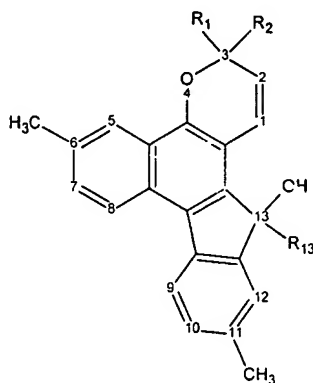
photochromic compounds. In particular, the coloration and discoloration kinetics of the (two or more) combined active photochromic compounds must be essentially identical. The same applies for their stability with time, and also for their compatibility with a single plastic or inorganic support.

- 5 Amongst the numerous photochromic compounds described in the prior art, benzopyrans or naphthopyrans are described in patents or patent applications U.S. Patents Nos. 3,567,605; 3,627,690; 4,826,977; 5,200,116; 5,238,981; 5,411,679; 5,429,744; 5,451,344; 5,458,814; 5,651,923; 5,645,767; 5,698,141; WO-A-95 05382; WO-A-96-14596; WO-A-97 21698 which are of the reduced formula below:



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Specifically, U.S. Patents Nos. 5,645,767 and 5,955,520 describe photochromic inden[2,1-f]naphtho[1,2-b]pyrans showing activated colors ranging from orange to blue-gray:



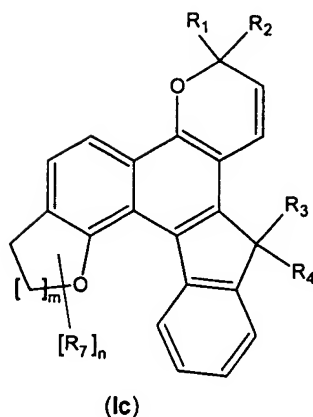
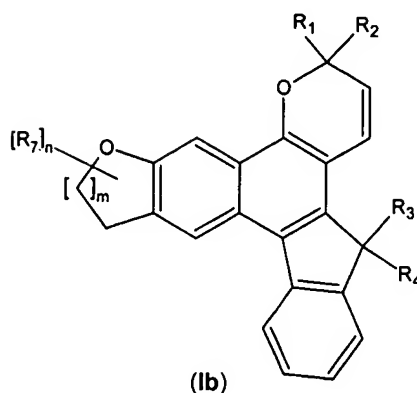
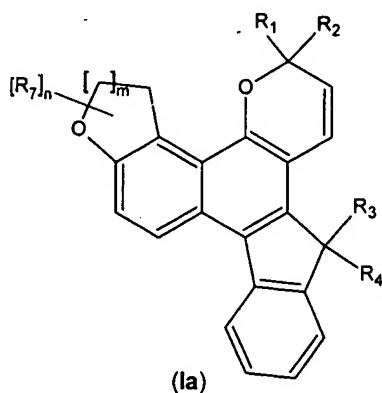
US 5,645,767

US 5,955,520

- Those photochromic materials are characterized by a major absorption of visible light in the 580 – 620 nm range coupled with a minor absorption in the 420 – 500 nm range.

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12. The photochromic naphthopyran of claim 1 wherein the naphthopyran has a



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formula selected from the group consisting of (Ia), (Ib), and (Ic) below, in which:
m is an integer 1 or 2,

R₁ and/or R₂, independently represent optionally substituted aryl or heteroaryl groups the basic structure of which is selected from phenyl, naphthyl, biphenyl, pyridyl, furyl, benzofuryl, dibenzofuryl, N--(C₁-C₆)alkylcarbazole, thienyl, benzothienyl, dibenzothienyl, julolidinyl groups; R₁ and/or R₂ advantageously representing a para-substituted phenyl group, said substituents are selected from hydrogen, alkyl, alkoxy, dialkylamino, diarylamino, or R₁ and R₂ together form an adamantyl group or norbornyl group or anthracenylidene group;
R₃ and R₄ are the same or different, and may represent independently a hydrogen, a hydroxy, a halogen,

a linear, branched, or cyclic alkyl group that comprises 1 to 6 carbon atoms,

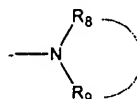
a $-OR_{20}$ group, wherein R_{20} is (C1-C3)alkyl, phenyl(C1-C3)alkyl, mono(C1-C3)alkylphenyl(C1-C3)alkyl, mono(C1-C3)alkoxyphenyl(C1-C3)alkyl, (C1-C3)alkoxy(C2-C4)alkyl, fluoro(C1-C3)alkyl, or chloro(C1-C3)alkyl,

an optionally substituted phenyl or benzyl group, said substituents being mono, di-, or tri-substituents, and selected from group R_{20} ,

a $-C(R_{21})_2X$ group, wherein X is hydroxy, alkoxy, benzyloxy, C1-C6 acyloxy, an ester group: $-COOR_{11}$, an amine or amide group: $-NH_2$, $-NHR_8$, $-N(R_8)_2$, $-CONH_2$, $-CONHR_8$, $-CON(R_8)_2$, R_{21} is hydrogen, C1-C6 alkyl, phenyl or naphthyl with C1-C6 alkyl or C1-C6 alkoxy substituents,

a polyether or polyurea residue,

or R_3 and R_4 together form a 5- to 7-member optionally substituted spiro-cyclic ring which can comprise at least one heteroatom selected from oxygen, sulfur, and nitrogen, and/or at least one substituent selected from the group consisting of a C1 to C6 alkyl group which is linear or branched, a C1 to C6 alkoxy group which is linear or branched, and an amine group of formula $-NH_2$, NHR_8 ,



the spiro-ring may be annelated with one or two benzene groups;

R_7 , which are identical or different, represent, independently

a hydrogen,

a linear or branched alkyl group which comprises 1 to 6 carbon atoms,

a cycloalkyl group comprising 3 to 7 carbon atoms,

a linear or branched alkoxy group comprising 1 to 6 carbon atoms,

a haloalkyl, halocycloalkyl, or haloalkoxy group corresponding to the alkyl, cycloalkyl, alkoxy groups above respectively, which are substituted with at least one halogen atom,

a linear or branched alkenyl or alkynyl group comprising 1-12 carbon atoms,

a linear or branched alkenoxy or alkynoxy group comprising 1-12 carbon atoms,

n is an integer from 0 to 2.

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13. A photochromic article comprising a polymeric layer containing a photochromic amount of a photochromic naphthopyran according to claim 1.

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14. A photochromic article comprising a polymeric layer containing a photochromic amount of a photochromic naphthopyran according to claim 2.

15. A photochromic article comprising a polymeric layer containing a photochromic amount of a photochromic naphthopyran according to claim 3.

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16. A photochromic article comprising a polymeric layer containing a photochromic amount of a photochromic naphthopyran according to claim 4.

17. A photochromic article comprising a polymeric layer containing a photochromic amount of a photochromic naphthopyran according to claim 9.

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18. A photochromic article comprising a polymeric layer containing a photochromic amount of a photochromic naphthopyran according to claim 10.

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19. A photochromic article comprising a polymeric layer containing a photochromic amount of a photochromic naphthopyran according to claim 11.

20. A photochromic article comprising a polymeric layer containing a photochromic amount of a photochromic naphthopyran according to claim 12.

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